



Research paper

Formation mechanism of layered double hydroxides in Mg^{2+} -, Al^{3+} -, and Fe^{3+} -rich aqueous media: Implications for neutralization in acid leach ore milling



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ABSTRACT

Hydrotalcite-like layered double hydroxides (HT-LDHs) are important due to their extensive use in catalysis, polymer science, medicine, refractory materials, and the remediation of contaminated waters. The inclusion of several cations and anions in their structure can result in complex formation mechanisms depending on the chemical nature of the respective species. A systematic evaluation of the formation mechanism of HT-LDH from $Mg^{2+}Al^{3+}Fe^{3+}$ -rich aqueous media at ambient conditions was conducted to determine formation pathways in natural settings and in conditions observed in ore milling processes. Neutralization from pH 1.7 to 12.5 (using NaOH) of individual M^{2+} and M^{3+} ions demonstrated that M^{3+} -hydroxides precipitate first, followed by M^{2+} -hydroxides in the order of $Fe(OH)_3$, $Al(OH)_3$, then $Mg(OH)_2$. The rate of formation accelerates as pH increases. The addition of M^{2+} ions to M^{3+} -hydroxides produces HT-LDH while the addition of M^{3+} ions to M^{2+} -hydroxides does not. HT-LDH precipitates immediately under alkaline conditions (pH = 13.2) with available $M^{2+} + M^{3+}$ ions, while formation progresses slowly as initially acidic conditions (pH = 1.7) are neutralized (to pH = 12.5) via the precipitation of M^{3+} -hydroxides and subsequently HT-LDH. This latter formation pathway is consistent with observations of the formation of MgFeAl HT-LDH during the neutralization process in an acid-leach process uranium mill: HT-LDH is first observed at pH ~ 6.4 and is dominant at pH ~ 8.0 or greater. At pH ≥ 6.4, HT-LDH is co-associated with Fe^{3+} -hydroxides. The early formation of M^{3+} -hydroxides and substitution by M^{2+} ions into the structure appear to govern the overall HT-LDH formation mechanism, with the resulting excess positive charge counterbalanced by CO_3^{2-} ions through atmospheric CO_2 dissolution.

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1. Introduction

Hydrotalcite-like layered double hydroxides (HT-LDHs) are the focus of broad ranging research due to their extensive use as adsorbents, as catalysts, and in pharmaceuticals, to name a few (Cavani et al., 1991; Othman et al., 2009; Paikaray et al., 2013). HT-LDHs are a group of minerals containing divalent ($M^{2+} = Mg^{2+}, Ni^{2+}, Fe^{2+}$, etc.) cations, trivalent ($M^{3+} = Al^{3+}, Fe^{3+}, Cr^{3+}$, etc.) cations, and interlayer anions ($A^{n-} = OH^-, Cl^-, NO_3^-, SO_4^{2-}, CO_3^{2-}$, etc.) that satisfy the general stoichiometry $[M^{2+}_1 - xM^{3+}_x(OH)_2]^{x+}(A^{n-}_{x/n}) \cdot mH_2O$, where x is $M^{3+} / (M^{2+} + M^{3+})$ (Cavani et al., 1991; Forano et al., 2006; Vaccari, 1998). Structurally, HT-LDH resembles brucite ($Mg(OH)_2$), with some M^{2+} substituted by M^{3+} resulting in an excess positive charge that is balanced by A^{n-} ; the free space not occupied by A^{n-} is filled by H_2O .

The structure of HT-LDH is dynamic (i.e., it can be destroyed by expelling interlayer H_2O via heating and reformed via interaction with anionic species) (Cavani et al., 1991; Zaneva and Stanimirova, 2004). HT-LDH formation is favored under alkaline conditions (Cavani et al., 1991; Klopogge et al., 2004; Paikaray and Hendry, 2014) and synthesis can be conducted through either urea hydrolysis or a hydroxyl ion supply (e.g., NaOH) (Duan and Evans, 2006; Othman et al., 2009). Although the former produces a product that has a greater degree of crystallinity due to slow nucleation (Naghash et al., 2008; Othman et al., 2009), the latter better represents the HT-LDH produced in natural systems (Cavani et al., 1991; Forano et al., 2006; Vaccari, 1998).

Studies into the mechanism of formation via substitution (i.e., either M^{2+} by M^{3+} or vice versa) of hydroxides that ultimately lead to the formation of HT-LDH are limited and the mechanisms of formation of HT-LDH appear complex. For example, we observed (unpublished data) that the addition of Mg^{2+} to an $Al(OH)_3$ precipitate yields HT-LDH, while the addition of Al^{3+} to a $Mg(OH)_2$ precipitate does not. However, both the titration of a cationic mixture of 0.15 M ($Al^{3+} + Mg^{2+}$) with 0.35 M NaOH and the titration of 0.35 M NaOH with 0.15 M ($Al^{3+} + Mg^{2+}$) yielded $MgAlCO_3$ -type HT-LDH (Fig. A1).

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Understanding the mechanism(s) of formation of HT-LDH during neutralization of aqueous phases containing M^{2+} and M^{3+} ions as they evolve from acidic (pH ~ 1.5) to highly alkaline conditions (pH > 10) is important with respect to ore milling processes that use acid leaching techniques. HT-LDHs have the ability to sequester potential contaminants in pore water in mine tailings derived from the mill process. For example, recent investigations into mineralogical controls in an acid-leach uranium mill in northern Saskatchewan, Canada show that (1) acidic (pH ~ 1) eluents after U extraction in the mill were enriched in Mg^{2+} , Al^{3+} , and Fe^{3+} ; (2) as the pH increased to pH 10 (via lime neutralization), the concentrations of these dissolved species dramatically decreased; and (3) HT-LDHs were observed in solid samples at pH > 6.0 (Gomez et al., 2013). The objective of the present study was to combine findings from this U mill and from synthetic batch testing to characterize the formation mechanism(s) and substitution dynamics of $MgAlFeCO_3$ -type HT-LDH under ambient conditions.

2. Experimental

Analytical reagent grade (>99%) chemicals and milli-Q water (18 M Ω ·cm) were used to produce all working solutions. All glassware was preconditioned in 10 vol% HNO_3 for ~4 h, then rinsed 4–5 times and immersed for >5 h in ultrapure milli-Q H_2O . All experiments were conducted under aerobic ambient conditions consistent with those in the mine tailings facility (MTF) neutralization process.

2.1. Experiment 1: effect of anionic strength on reaction rate

Solutions of 0.5 M Mg^{2+} , 0.125 M Al^{3+} , and 0.125 M Fe^{3+} were prepared using $MgCl_2 \cdot 6H_2O$, $AlCl_3 \cdot 6H_2O$, and $FeCl_3 \cdot 6H_2O$, respectively. Individual solutions (50 mL) were titrated with 50 mL of 0.5, 1.0, or 2.5 M NaOH (pH 13.2, 13.3, and 13.6, respectively) to characterize the effects of anionic strength on precipitation kinetics. The solution pH was measured throughout the ~60 min titrations (after every 0.2 mL addition). Initial and final precipitates were immediately collected for characterization and repeatedly washed through centrifugation to remove impurities (e.g., Cl^-) and air dried.

2.2. Experiment 2: dynamics of cation substitution

Two experiments were conducted to determine which substitution process favors the formation of HT-LDH (i.e., M^{2+} by M^{3+} or vice versa). These experiments were conducted using (a) 50 mL of M^{2+} (0.5 M $MgCl_2 \cdot 6H_2O$ + 1.0 M NaOH) titrated with 50 mL of M^{3+} (0.125 M $AlCl_3 \cdot 6H_2O$ + 0.125 M $FeCl_3 \cdot 6H_2O$) and (b) 50 mL of M^{3+} (0.125 M $AlCl_3 \cdot 6H_2O$ + 0.125 M $FeCl_3 \cdot 6H_2O$ + 1.0 M NaOH; pH = 12.7) titrated with 50 mL of 0.5 M $MgCl_2 \cdot 6H_2O$ (pH = 5.1). pH changes were monitored with each 0.2 mL addition of titrant. In both cases, initial and final products were collected and processed as described above prior to analysis. The precipitate resulting from titration (b) was aged at 65 °C for 24 h under normal atmospheric conditions to increase its degree of crystallinity, in accordance with routine practices (Cavani et al., 1991; Forano et al., 2006; Paikaray et al., 2013).

2.3. Experiment 3: formation pathways

To determine the formation mechanism of HT-LDH directly from an alkaline medium, 100 mL of 1.0 M NaOH was titrated with 0.5 M $MgCl_2 \cdot 6H_2O$ + 0.125 M $AlCl_3 \cdot 6H_2O$ + 0.125 M $FeCl_3 \cdot 6H_2O$ to pH 12.2. The pH was measured after the addition of each 0.2 mL of titrant. No plateaus were observed in the pH profile, so only initial and final products were collected, washed, centrifuged, and dried as described above.

The reverse titration was also conducted, wherein 50 mL M^{2+} + M^{3+} solution (0.5 M $MgCl_2 \cdot 6H_2O$ + 0.125 M $AlCl_3 \cdot 6H_2O$ + 0.125 M $FeCl_3 \cdot 6H_2O$; M^{2+} + M^{3+} = 0.75 M; M^{2+}/M^{3+} = 2) was titrated with

100 mL of 1.0 M NaOH to pH 12.5. The pH was measured after the addition of each 0.2 mL of titrant. Based on observed pH plateaus, a total of six precipitates were collected in separate experiments (i.e., titration was stopped and solid samples were collected). The solids were washed, separated, and dried as described above. Air dried samples were stored at room temperature for subsequent analyses.

2.4. Experiment 4: transformation kinetics

The stability of M^{2+} -hydroxides in M^{3+} -rich aqueous media and M^{3+} -hydroxides in M^{2+} -rich aqueous media was examined by conducting an aging experiment. The M^{3+} - and M^{2+} -hydroxides used in this experiment were precipitates formed in Experiment 1 upon the titration of the Al^{3+} -, Fe^{3+} -, and Mg^{2+} -rich solutions with 0.5 M NaOH. Two sets of tests were conducted. In the first set, 1 g $Mg(OH)_2$ was equilibrated in ~150 mL of 0.125 M $AlCl_3 \cdot 6H_2O$ + 0.125 M $FeCl_3 \cdot 6H_2O$ solution. The pH was then raised to either 9 or 12 (using NaOH) and the samples aged for 30 d at room temperature under ambient conditions. In the second set of tests, 1 g M^{3+} precipitate (0.5 g $Al(OH)_3$ + 0.5 g $Fe(OH)_3$) was equilibrated in ~150 mL of 0.5 M $MgCl_2 \cdot 6H_2O$. The pH was then raised to either 9 or 12 and the samples aged as noted above. For both sets of tests, the pH was monitored and adjusted 5–6 times per day throughout the aging period. Control experiments were also conducted (no pH adjustment). Samples were collected after 15 and 30 d to characterize changes in mineralogy with aging. Solid samples were purified as described above prior to analysis.

2.5. Samples from the Key Lake mill

Raffinate neutralization products were collected from the Key Lake acid-leach uranium mill in Northern Saskatchewan, Canada. After extraction of uranium an acidic pregnant solution (termed raffinate) with enriched non-toxic and toxic elements (e.g., Fe, Al, Mg, As, Mo, Ni) is subjected to bulk neutralization process. Precipitates and solutions formed during the neutralization process were collected directly from the Key Lake mill site on August 2011 as reported by Gomez et al. (2013). Only selected precipitates at pH 4.3, 4.4, 6.4 and 10.1 are considered here for understanding HT-LDH formation conditions.

2.6. Analytical techniques

Solid samples (powdered) were mounted on glass slides using methanol and dried for ~30 min at room temperature for analysis by X-ray diffraction (XRD) with a PANalytical Empyrean X-ray diffractometer at 40 kV and 45 mA using Co K α radiation (λ = 1.78901 Å) between 10 and 80 °2 θ at a 0.02° sec⁻¹ step size and an 80 sec step time. Peak indexing was performed using PowderX software and compared with previous studies. The lattice parameters 'c' and 'a' of the HT-LDH were calculated from the diffraction plane positions of $d_{(003)}$, $d_{(006)}$, $d_{(009)}$, and $d_{(110)}$ according to

$$c = d_{(003)} + 2d_{(006)} + 3d_{(009)} \quad (1)$$

$$a = 2d_{(110)} \quad (2)$$

and considering the peaks at ~13, ~27, ~40 °2 θ and first peak of the doublet at ~70–72 °2 θ corresponding to ~7.6, ~3.8, ~2.6 and ~1.5 Å (Cavani et al., 1991; Rives and Kannan, 2000) belonging to a hexagonal crystal system with 3R symmetry. To be consistent with previous studies (Kannan and Swamy, 1997; Naghash et al., 2008; Parida et al., 2012; Zhao et al., 2002), the crystallite size along the c-axis was determined from the full width at half maximum (FWHM) values of $d_{(003)}$ plane using Scherrer's formula,

$$t = \frac{K\lambda}{\beta \cos \theta_{hkl}} \quad (3)$$

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